

Assignment of 9250–13000 cm⁻¹ water vapor absorption spectrum

L.P. Vorob'eva, B.A. Voronin, and O.V. Naumenko

*Institute of Atmospheric Optics,
Siberian Branch of the Russian Academy of Sciences, Tomsk*

Received October 14, 2003

Assignment of the water vapor absorption spectrum in the 9250–13000 cm⁻¹ spectral region recorded by Mérienne with co-workers [J. Quant. Spectrosc. Radiat. Transfer **82**, 99–117 (2003)] is presented, which is based on the *ab initio* calculation and application of the expert system for automatic assignment of rovibrational spectra. In addition to the existing data, 1938 lines were assigned. Careful analysis of lines left unassigned has shown that some of them may be artifacts accompanying recording of a strong line. Comparison of the results obtained with the HITRAN-2000 data and recent publications is performed.

Introduction

Water vapor absorbs about 70% of the solar radiation in the Earth's atmosphere. In this connection, detailed and precision absorption spectra of the H₂O molecule and its isotopic modifications are of primary importance for provision of atmospheric sensing problems. In recent years, a lot of experimental and theoretical papers devoted to analysis of water vapor absorption spectra were published.^{1–9}

At the same time, simulation and assignment of water vapor absorption spectra present a rather complicated problem, especially, in the near-IR and visible regions, where the spectrum is due to transitions to highly excited rotational-vibrational (RV) states. The problem is that the H₂O molecule is a light asymmetric top with strong non-rigidity effects accompanying excitation of the large-amplitude bending vibration. Traditional approaches to description of rovibrational spectra based on the assumption of small vibrations turn out inefficient in this case, since they lead to poorly converging series in matrix elements of the Hamiltonian.

The use of the divergent series summation technique to calculate high-excited energy levels of H₂O molecule¹⁰ significantly improves the accuracy of reconstruction and prediction of experimental data within the framework of the method of effective RV Hamiltonian. However, water vapor absorption spectra in the near-IR and, especially, visible region are weak and hard to record. The deficit of the experimental information for RV states comprising a resonating polyad hampers a complete realization of the effective Hamiltonian method, which assumes retrieval of rotational, centrifugal distortion, and resonance constants, as well as dipole moment parameters from the fitting to experimental line positions and intensities.

In addition to the above problems, the strength and number of anharmonic and RV resonances

between not only members of the same polyad, but also between resonating polyads increase with growing vibrational excitation.¹¹ In such a case, the dimension of the inverse problem on retrieval of spectroscopic parameters increases considerably, as well as the number of dark states not included in the consideration.

In connection with the difficulties arising when using the effective Hamiltonian method for high-excited states of water vapor, of great interest are *ab initio* and variational calculations, whose accuracy was significantly improved in recent years.^{12–14} The most accurate *ab initio* calculation of the water vapor absorption spectrum is now the Partridge–Schwenke (PS) calculation.^{12,13}

This paper presents the complete assignment of the recently published⁸ water vapor absorption spectrum in the wide spectral region 9250–13000 cm⁻¹. The assignment was carried out based on the PS synthetic spectrum and calculations by the effective Hamiltonian method.

1. Experimental data and assignment procedure

The water vapor absorption spectrum was recorded on a Fourier Transform (FT) spectrometer coupled with a multipass cell, giving an equivalent absorbing path up to 602 m long, at the temperature of 292 K (Ref. 8) and the resolution of 0.03–0.06 cm⁻¹. A total of 7061 water vapor absorption lines were recorded, and 4725 of them were assigned. For each line Ref. 8 gives the measured intensities, and for some lines the air broadening and self-broadening coefficients are presented, along with the pressure-induced shifts.

In fact, Mérienne with co-workers⁸ did not identify the spectrum, but only assigned lines from the HITRAN-2000 database. As a result, 2336 lines were left unassigned. Our task was to carry out a complete identification of the spectrum and to

compile the detailed database on water vapor absorption in the 9250–13000 cm^{-1} region. The process of the identification involved the usage of an expert system for automatic line assignment in rovibrational molecular spectra.¹⁵

The expert system for spectral line assignment is based on the Ritz–Rydberg combination principle and employs the pattern recognition theory for selection of the true combination difference in the spectrum. It takes into account the proportionality between calculated and experimental intensities, line number in the combination difference, the accuracy of fulfillment of the combination rule, and some other informative indices for correct choice.¹⁵ The system records the assignment, proposed by it and confirmed by the operator, into a database; and the corresponding “upper” experimental level, determined as an average over a set included in the combination difference, is stored into the database of energy levels.

The expert system in its operation uses a list of experimental lines and intensities, as well as the synthetic absorption spectrum in the region under study. The quality of the synthetic spectrum is a very important factor for its successful operation, especially, when we deal with interpretation of weak absorption lines corresponding to transitions to highly excited RV states. Such lines usually have no combination difference partners, and their assignment fully depends on the accuracy of the synthetic spectrum.

In this work, the synthetic absorption spectrum of H_2^{16}O , H_2^{17}O , H_2^{18}O , and HDO molecules was taken from the Partridge–Schwenke *ab initio* calculation.^{12,13} A high accuracy of the calculation was confirmed in many studies (see, for example, Refs. 16–18), but a disadvantage of this calculation was mentioned as well, namely, in many cases the levels with different values in the PS database have the same RV assignment. Thus, for example, the states (300) and (310) have a double set of levels in the PS database, while for the states (102) and (112) the levels are lacking. For the spectral region under study, the mean accuracy of the PS calculation can be assessed as $< 0.1 \text{ cm}^{-1}$ for line positions and $< 10\%$ for intensities.

To correct the PS calculation by the effective Hamiltonian method, we have carried out approximate fitting of spectroscopic parameters for all vibrational states, transitions to which fall within the region under study. Since the water vapor molecule experiences a strong centrifugal distortion, we used the operator expressed through Pade–Borel approximants as an effective rotational Hamiltonian.^{19,20} In the fitting of energy levels we have stopped at the standard deviation of 0.03–0.05 cm^{-1} . This accuracy was sufficient both for correction of the RV assignment of the Partridge–Schwenke spectrum and for adequate modeling of experimental intensities.

Finally, we succeeded in interpretation of most unassigned lines in the spectrum from Ref. 8: 1938 of

2336 were assigned. In addition, some lines incorrectly interpreted in Ref. 8 were revised.

2. Results and discussion

The resulting information on assignment of the water vapor absorption spectrum in the 9250–13000 cm^{-1} region is summarized in Table 1, which lists the vibrational states for the H_2^{16}O isotopic species, the transitions to which are assigned in the spectrum, as well as integral intensities of vibrational bands. Note that experimental integral intensities of the bands were obtained as sums of intensities of all absorption lines assigned to this band. In the case that an experimental line was formed by several lines belonging to different bands, it was included in the integral intensity of the band corresponding to the strongest multiplet component.

Besides transitions corresponding to H_2^{16}O absorption, we have interpreted tens and even hundreds of lines corresponding to absorption of isotopic species: H_2^{17}O , H_2^{18}O , and HDO. Table 2 exemplifies the content of the database on identification of the experimental water vapor absorption spectrum. Figure 1 depicts the fragments of the experimental⁸ and synthetic (PS) spectra; a good agreement between the spectra is clearly seen.

In addition, Table 1 gives the integral intensities of water vapor vibrational bands from the HITRAN-2000 database and those estimated based on the Partridge–Schwenke calculation. We can see a good agreement between the calculation and two sets of experimental integral intensities for strong and moderate bands. At the same time, integral intensities of some weak bands in the HITRAN database are underestimated, especially, in the longwave part of the spectrum, while lines belonging to the bands (140)–(000), (230)–(000), (060)–(000), (070)–(000), and others are lacking at all. It should be also noted that we observed a large number of wrong assignments of RV lines in the HITRAN-2000 database.

Figure 2 compares two experimental spectra: the analyzed one and that from the HITRAN database with the calculated PS spectrum in the region of 9520–9700 cm^{-1} . We can see that the new experimental spectrum includes much more weak absorption lines. Almost simultaneously with the spectrum from Ref. 8 the water vapor absorption spectrum in the region of 9520–10010 cm^{-1} was studied by the methods of high-sensitivity intracavity spectroscopy.²¹ This spectrum includes several tens of extra weak lines as compared to the spectrum from Ref. 8.

The overwhelming majority of 398 unassigned absorption lines are very weak, and their experimental intensities are given with large errors. We believe that most of these lines (about 260) are, likely, noise or artifacts. It should be mentioned that after some discussions Mérienne with co-workers excluded many of these lines in question from the final list.

Table 1. Integral intensities I of H_2^{16}O vibrational absorption bands in the region 9250–13000 cm^{-1}

E_v, cm^{-1}		$V_1 V_2 V_3$	$I, \text{cm}^{-2}\cdot\text{atm}^{-1}$		Line number	$I, \text{cm}^{-2}\cdot\text{atm}^{-1}$		Line number	$I, \text{cm}^{-2}\cdot\text{atm}^{-1}$		Line number
Calc. ¹³	Exp. ²²		Calc. ¹³	Exp. ⁸		Exp. ⁹	HITRAN-2000				
7542.51	7542.4366	0 5 0	1.92E-07	1.87E-07	2	0	0				
8274.05	8273.9757	1 3 0	3.64E-06	3.64E-06	7	2.85E-06	1				
8373.90	8373.8521	0 3 1	3.04E-06	2.72E-06	17	1.19E-06	3				
8761.66	8761.5820	2 1 0	2.01E-05	2.03E-05	44	1.62E-05	7	1.80E-05		4	
8807.04	8807.0006	1 1 1	1.44E-04	1.33E-04	78	1.39E-04	52	1.12E-04		38	
8870.59	8869.9538	0 6 0	4.73E-05	5.08E-05	35	3.86E-05	8				
9000.11	9000.1365	0 1 2	7.32E-04	6.87E-04	111	6.58E-04	65	5.74E-04		43	
9724.40		1 4 0	8.04E-05	8.33E-05	232	4.60E-05	108				
9833.63	9833.5845	0 4 1	1.07E-03	1.14E-03	387	1.11E-03	322	1.12E-03		204	
10087.14		0 7 0	1.28E-04	1.35E-04	57	0	0				
10284.35	10284.3670	2 2 0	2.14E-03	2.05E-03	350	2.00E-03	295	2.03E-03		202	
10328.67	10328.7309	1 2 1	5.98E-02	6.03E-02	568	6.22E-02	517	5.98E-02		452	
10521.77	10521.7553	0 2 2	2.72E-03	2.76E-03	324	2.67E-03	278	2.72E-03		202	
10599.68	10599.6863	3 0 0	3.94E-02	4.01E-02	561	4.18E-02	550	4.25E-02		479	
10613.40	10613.3547	2 0 1	4.60E-01	4.65E-01	699	4.61E-01	697	4.63E-01		638	
10868.89	10868.8757	1 0 2	1.50E-02	1.53E-02	465	1.52E-02	487	1.50E-02		350	
11032.46	11032.4058	0 0 3	5.32E-02	5.32E-02	475	5.45E-02	487	5.32E-02		435	
11099.24		1 5 0	1.10E-07	9.67E-08	1	2.80E-05	7				
11242.78		0 5 1	1.23E-04	1.16E-04	26	9.52E-05	38				
11767.52	11767.3900	2 3 0	1.62E-04	1.59E-04	72	1.93E-04	156				
11813.23	11813.2072	1 3 1	1.32E-03	1.29E-03	274	1.34E-03	378	1.02E-03		239	
12007.92		0 3 2	8.71E-05	9.30E-05	56	1.21E-04	146	1.12E-06		1	
12139.36	12139.3154	3 1 0	1.58E-03	1.49E-03	179	1.55E-03	272	1.37E-03		231	
12151.32	12151.2548	2 1 1	3.61E-02	3.26E-02	394	3.38E-02	530	3.25E-02		511	
12407.65	12407.6621	1 1 2	1.24E-03	1.31E-03	188	1.37E-03	288	1.28E-03		215	
12565.01	12565.0071	0 1 3	2.73E-03	2.50E-03	204	2.48E-03	275	2.40E-03		248	

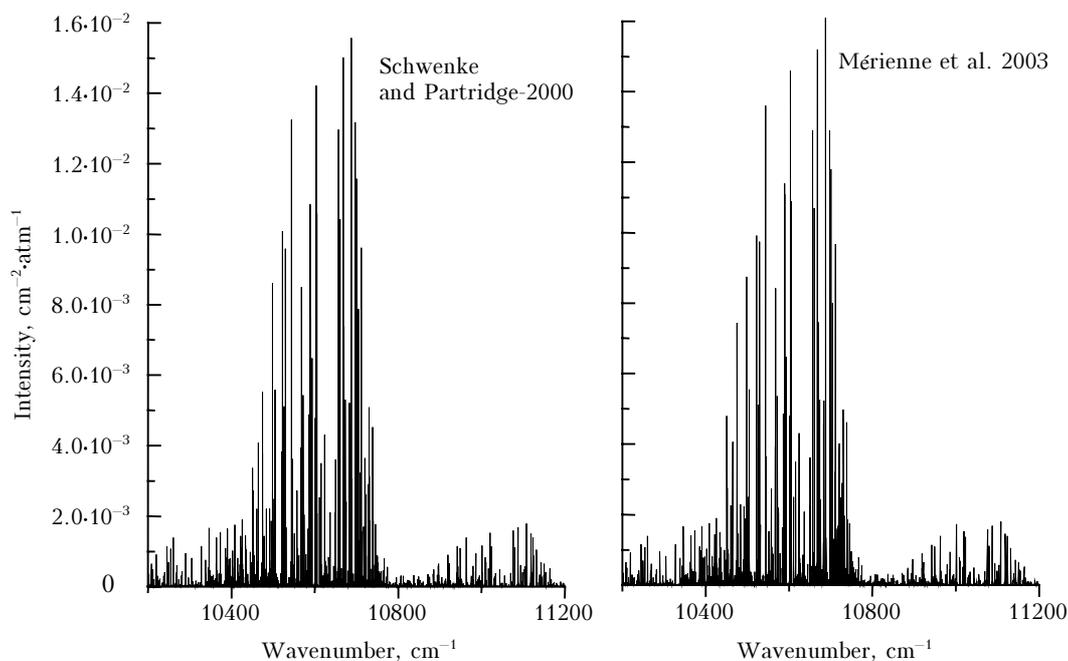
**Fig. 1.** Fragment of water vapor absorption spectrum: Partridge–Schwenke *ab initio* calculation¹³ (left) and experimental spectrum⁸ (right).

Table 2. Fragment of the database on water vapor absorption in the region 9250–13000 cm⁻¹

Wavenumber, cm ⁻¹	$I, \text{cm}^{-2} \cdot \text{atm}^{-1}$		$V_1 V_2 V_3$	$J K_a K_c$	$J K_a K_c$	$V_1 V_2 V_3$	$I, \text{cm}^{-2} \cdot \text{atm}^{-1}$ [Ref. 13]	$J K_a K_c$	$J K_a K_c$
	Exp. ⁸	Calc. ¹³	This work			Ref. 9			
9506.4175	6.89E-07	7.5E-07	0 1 2	10 3 8	9 0 9	0 0 3	1.8E-08	4 1 4	3 1 3
9518.8507	2.30E-07	2.2E-07	1 4 0	9 0 9	10 1 10	1 4 0	0	4 1 4	5 2 3
9564.2077	6.64E-07	6.3E-07	1 4 0	7 0 7	8 1 8				
9616.8336	4.21E-07	3.3E-07	1 4 0	5 1 5	6 0 6				
9621.9530	6.92E-08	7.9E-08	1 4 0	8 2 7	9 1 8				
9791.4661	1.68E-07	1.5E-07	1 4 0	4 2 2	5 1 5				
9812.1687	7.66E-08	8.5E-08	1 4 0	6 2 4	7 1 7	1 3 1	0	5 4 1	6 6 0
9834.0068	2.00E-07	1.7E-07	1 4 0	7 2 5	8 1 8				
9834.2015	1.51E-07	1.2E-07	1 4 0	6 3 3	7 2 6				
		1.9E-08	19_1 0 2	3 1 2	4 2 3				
9861.1166	1.52E-06	1.4E-07	1 4 0	4 3 1	5 2 4	1 4 0	1.4E-07	4 3 1	5 2 4
		1.4E-06	1 4 0	7 0 7	6 1 6				
9872.4899	8.75E-08	7.8E-08	1 4 0	3 2 2	3 1 3				
9875.9359	3.12E-07	3.5E-07	1 4 0	8 0 8	7 1 7				
9882.2199	6.37E-08	6.6E-08	1 4 0	9 4 5	10 3 8				
9889.2363	5.88E-07	6.6E-07	1 4 0	9 0 9	8 1 8				
9892.8219	1.50E-07	1.1E-07	0 4 1	10 5 5	11 5 6				
		3.5E-08	19_1 0 2	4 1 4	5 1 5				
9894.4142	2.02E-07	2.0E-07	1 4 0	9 1 9	8 0 8	0 4 1	5.2E-09	10 3 8	10 3 7
9897.1991	3.69E-08	5.3E-08	1 4 0	11 1 11	10 0 10				
9899.8742	8.75E-08	7.9E-08	2 2 0	9 3 7	10 4 6				
9901.3916	1.14E-07	1.2E-07	1 4 0	10 0 10	9 1 9	1 1 1	0	18 6 12	17 2 15
9998.6235	2.73E-07	3.0E-07	1 4 0	10 3 8	11 0 11	1 2 1	0	8 3 5	7 7 0
10014.7407	6.64E-08	5.7E-08	2 2 0	11 2 9	12 3 10	1 1 1	0	16 4 12	15 0 15
10061.9348	1.31E-07	1.3E-07	1 2 1	11 3 8	12 3 9	1 2 1	0	9 6 3	9 8 2
10068.8991	7.96E-06	2.1E-06	2 0 1	7 4 4	8 6 3				
		5.2E-06	1 2 1	10 1 10	11 1 11				
		8.8E-07	1 2 1	10 4 6	11 4 7	1 2 1	8.8E-07	10 4 6	11 4 7
10081.5609	1.06E-06	3.3E-07	2 0 1	10 2 8	11 4 7	2 0 1	3.3E-07	10 2 8	11 4 7
		6.5E-07	2 2 0	8 1 7	9 2 8				
10098.3927	6.20E-07	6.2E-07	1 4 0	5 4 1	5 3 2	0 2 2	3.1E-09	8 4 5	8 7 2
10103.0060	6.89E-07	5.0E-07	1 2 1	10 1 10	10 1 9				
		1.3E-07	1 4 0	8 4 5	8 3 6	1 4 0	1.3E-07	8 4 5	8 3 6
10104.8029	3.79E-06	2.6E-06	2 2 0	7 1 7	8 0 8				
		1.1E-06	3 0 0	8 6 3	9 7 2	3 0 0	1.1E-06	8 6 3	9 7 2
10114.9886	6.74E-08	4.1E-08	1 2 1	12 2 11	12 2 10	0 4 1	0	13 5 9	13 5 8
10126.4617	2.46E-07	2.7E-07	0 4 1	10 2 9	9 2 8	0 3 1	0	16 10 6	15 6 9
10128.9592	1.04E-05	5.3E-06	1 2 1	9 4 6	10 4 7				
		4.7E-06	2 2 0	6 0 6	7 1 7	2 2 0	4.7E-06	6 0 6	7 1 7
10138.2862	1.16E-06	7.0E-07	1 2 1	8 3 5	8 5 4				
		3.3E-07	0 4 1	4 3 1	4 1 4	0 4 1	3.3E-07	4 3 1	4 1 4
10139.8960	8.68E-08	9.6E-08	0 6 0	7 6 1	7 5 2	3 0 0	0	14 2 12	15 3 13
10145.8429	5.83E-08	9.7E-08	0 2 2	11 5 6	12 6 7	1 2 1	0	12 2 10	11 6 5
10169.2117	2.58E-05	1.6E-05	0 4 1	5 5 1	5 5 0				
		5.3E-06	0 4 1	5 5 0	5 5 1	0 4 1	5.3E-06	5 5 0	5 5 1
10175.2232	4.96E-07	4.5E-07	0 7 0	7 1 6	8 2 7	1 3 1	3.2E-08	4 4 1	5 4 2
10218.8301	6.05E-06	2.5E-06	1 2 1	3 1 2	3 3 1				
		1.7E-06	2 2 0	3 1 3	3 2 2	2 2 0	1.7E-06	3 1 3	3 2 2
10235.9931	1.06E-06	1.1E-06	18_1 2 1	2 2 0	3 2 1	2 3 0	0	7 2 5	8 1 8
10236.2050	2.53E-07	2.1E-07	2 2 0	10 4 6	11 3 9				
10259.3545	6.74E-08	6.6E-08	18_0 2 2	5 4 1	6 5 2	1 2 1	0	5 5 1	5 5 2
10264.2599	4.98E-07	4.0E-07	1 2 1	5 1 5	4 3 2	1 0 2	0	11 6 6	12 7 5
10264.4413	6.87E-07	4.1E-07	1 3 1	2 1 2	1 1 1				
		5.0E-08	1 3 1	5 2 3	5 2 4				
		1.6E-07	17_1 2 1	1 0 1	2 0 2	1 2 1	1.6E-07	1 0 1	2 0 2
10325.1494	2.70E-05	2.8E-05	2 0 1	7 1 7	7 3 4	2 2 0	2.8E-07	3 1 2	2 2 1
10441.6178	1.20E-05	1.1E-05	1 2 1	6 2 5	6 0 6	1 0 2	8.1E-07	7 1 7	8 2 6
10642.1393	9.47E-06	1.2E-05	3 0 0	7 3 4	6 4 3	1 0 2	0	6 5 1	6 6 0
10720.9305	2.48E-05	2.5E-05	0 2 2	4 3 2	3 2 1	3 0 0	5.5E-07	6 4 2	7 1 7
10725.8706	2.73E-04	1.9E-04	2 0 1	8 5 3	7 5 2				
		2.6E-05	2 0 1	9 6 4	8 6 3				
		3.4E-05	3 0 0	9 1 9	8 0 8				
		1.6E-05	3 0 0	8 1 7	7 2 6	3 0 0	1.6E-05	8 1 7	7 2 6
10761.4361	3.84E-05	3.5E-05	3 0 0	10 3 8	9 2 7	2 0 1	5.0E-05	12 1 12	11 1 11

Note. I stands for line intensity. Numbers 17_, 18_, 19_ correspond to H₂¹⁷O, H₂¹⁸O, and HDO, respectively. The zero value of the calculated intensity means that the calculated value is less than 10⁻⁹ cm⁻²·atm⁻¹.

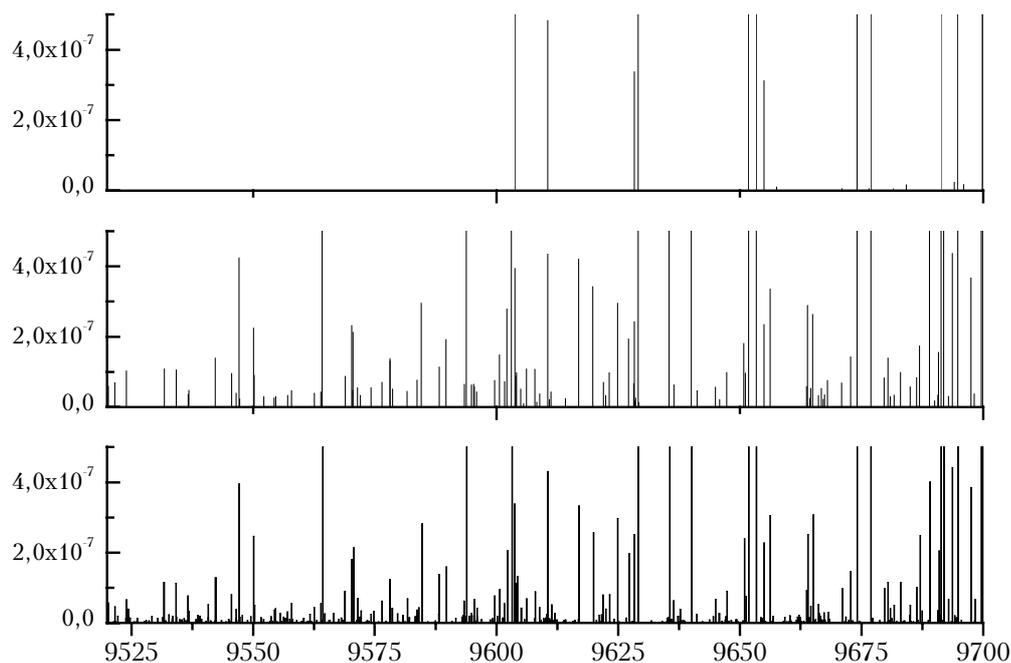


Fig. 2. Comparison of two experimental (HITRAN-2000 and Mérienne et al.⁸) spectra with the Partridge–Schwenke *ab initio* calculation.¹³

It seems interesting to discuss here the problem of so-called artifacts. The problem is that in Fourier Transform spectra a regular structure of peaks is often observed just near ($\leq 0.1 \text{ cm}^{-1}$) strong lines. Sometimes these peaks are misinterpreted as lines. These false lines may have relatively strong intensities. In the spectrum under analysis we observed tens of such artifacts. For example, near three strong lines: 10424.4881 , 10551.7923 , and $10708.2035 \text{ cm}^{-1}$ with the intensities of $5.95 \cdot 10^{-4}$, $1.53 \cdot 10^{-3}$, and $1.32 \cdot 10^{-3} \text{ cm}^{-2} \cdot \text{atm}^{-1}$, respectively, the list of lines⁸ included three relatively strong lines: 10424.5370 , 10551.8531 , and $10708.2612 \text{ cm}^{-1}$ with the intensities of $5.18 \cdot 10^{-5}$, $1.98 \cdot 10^{-5}$, and $1.19 \cdot 10^{-5} \text{ cm}^{-2} \cdot \text{atm}^{-1}$. These lines were unassigned, because they had no analogs in the PS calculation, which, nevertheless, permitted easy assignment of even very weak lines at the level of 10^{-7} – $10^{-8} \text{ cm}^{-2} \cdot \text{atm}^{-1}$. These lines also were not observed in the very detailed experimental spectrum recorded later in Ref. 9. It is quite probable that these lines are artifacts.

Reference 9 was published once we have completed assignment of the spectrum from Ref. 8. Tolchenov with co-workers⁹ considered the water vapor spectrum in the region 9000 – 12700 cm^{-1} , 7923 lines were recorded, and 7156 of them were assigned. The spectra from Refs. 8 and 9 complement each other in some sense: the data of Ref. 8 are more detailed in the longwave part of the spectrum, while the spectrum from Ref. 9 includes more lines in the shortwave part. Comparison between our interpretation of the spectrum⁸ and data from Ref. 9 have shown them to coincide for most lines.

Nevertheless, more than 200 lines were incorrectly or not completely interpreted in Ref. 9. Most lines unassigned in Ref. 9 are successfully identified by us in this work (provided they are in the list of lines⁸). Table 2 compares the assignments of this work and Ref. 9 for some fragment of the spectrum. It is seen that in Ref. 9 experimental lines are assigned to calculated PS transitions, whose intensities orders of magnitude differ from the experimental data, while in our interpretation the calculated PS intensities agree well with the experimental ones.

From comparison of the final line lists of this work and Ref. 9, we can clearly see the benefits of using the automatic expert system for detailed identification of a spectrum. This system performs the fast, reliable, and detailed identification. Up to three assignments are provided for every experimental line, while in Ref. 9 experimental lines have a single assignment.

In Ref. 9 the first stage of identification in the automatic mode involved so-called “trivial” assignments, that is, assignments of transitions to known upper experimental levels. The lines, for which at least one trivial assignment was found, were immediately excluded from consideration without checking the agreement between the calculated and experimental intensities. Finally, the resulting line list of Ref. 9 often includes lines, which have only one of two or three needed assignments, and this one may correspond to the weakest component of the multiplet. This is clearly demonstrated by the strong experimental line $10725.8706 \text{ cm}^{-1}$ (see Table 2) with the intensity of $2.73 \cdot 10^{-4} \text{ cm}^{-2} \cdot \text{atm}^{-1}$. This line, in

fact, is a superposition of four lines, while in Ref. 9 it is assigned to the weakest component of the quartet, whose intensity is tenfold as low as the measured one.

Table 1 gives the integral intensities of vibrational bands from Ref. 9 calculated as the sums of experimental intensities of the corresponding transitions in the region 9200–13000 cm^{-1} . As was already mentioned, the data of Ref. 9 in the longwave part of the spectrum are less detailed than the line list from Ref. 8; therefore, the integral intensities of the bands calculated by the data of Ref. 9 are markedly lower in this spectral interval. In the shortwave part, to the contrary, the spectrum from Ref. 9 includes more lines than that from Ref. 8, but the integral intensities estimated by the data from Ref. 9 usually only slightly differ from those estimated by the data from Ref. 8. This indicates that extra lines in Ref. 9 are very weak, and their total contribution to the integral intensity is low.

To be noted is the remarkable discrepancy between the integral intensities of the bands (150)–(000) and (070)–(000) estimated by the data from Refs. 8 and 9. Transitions to the highly excited state (070) borrow intensity through the HEL-resonance from lines – resonance partners belonging to the bands (220)–(000) and (121)–(000) [Ref. 11]; therefore, very weak line (070)–(000) has a marked intensity. In Ref. 9, the transitions to the (070) state are misassigned as belonging to the band (150)–(000). This seems to be a rather crude error, because the centers of the (150)–(000) and (070)–(000) bands are spaced by more than 1000 cm^{-1} (see Table 1).

In general, the comparison of the experimental accuracies in Refs. 8 and 9 gives the impression that line positions in Ref. 9 are, on the average, more accurate than in Ref. 8, while intensities in Ref. 9 seem, on the average, more rough than in Ref. 8.

Conclusion

The water vapor absorption spectrum in the region of 9250–13000 cm^{-1} has been completely interpreted based on the use of the highly accurate *ab initio* Partridge–Schwenke calculation and the automatic expert system for interpretation of rotational-vibrational spectra. A detailed database on absorption by water vapor and its isotopic species in this spectral region have been compiled.

Critical analysis of weak lines left unassigned in the experimental spectrum⁸ has allowed most of them to be excluded from the resulting list as noise or artifacts. The comparison of our identification of the spectrum from Ref. 8 with the results of the recently published Ref. 9 and the HITRAN-2000 database has shown that our assignment is most complete and accurate. At the same time, to obtain a more detailed list of experimental water vapor absorption lines in the region 9000–13000 cm^{-1} , all three experimental data sets mentioned above should be joined correctly.

Acknowledgments

This work was supported, in part, by the Russian Foundation for Basic Research (Grants No. 03–07–06065–mas, No. 02–07–90139, and No. 02–03–32512).

References

1. P.-F. Coheur, S. Fally, M. Carleer, C. Clerbaux, R. Colin, A. Jenouvrier, M.-F. Mérianne, C. Hermans, and A.C. Vandaele, *J. Quant. Spectrosc. Radiat. Transfer* **74**, 493–510 (2002).
2. L.R. Brown, R.A. Toth, and M. Dulick, *J. Mol. Spectrosc.* **212**, 57–82 (2002).
3. R. Schermaul, R.C.M. Learner, D.A. Newnham, R.G. Williams, J. Ballard, N.F. Zobov, D. Belmiloud, and J. Tennyson, *J. Mol. Spectrosc.* **208**, 32–42 (2001).
4. R. Schermaul, R.C.M. Learner, A.A.D. Canas, J.W. Brault, O.L. Polyansky, D. Belmiloud, N.F. Zobov, and J. Tennyson, *J. Mol. Spectrosc.* **211**, 169–178 (2002).
5. R. Schermaul, R.C.M. Learner, D.A. Newnham, J. Ballard, N.F. Zobov, D. Belmiloud, and J. Tennyson, *J. Mol. Spectrosc.* **208**, 43–50 (2001).
6. M. Tanaka, J.W. Brault, and J. Tennyson, *J. Mol. Spectrosc.* **216**, 77–80 (2002).
7. R.N. Tolchenov, J. Tennyson, J.W. Brault, A.A.D. Canas, and R. Schermaul, *J. Mol. Spectrosc.* **215**, 269–274 (2002).
8. M.-F. Mérianne, A. Jenouvrier, C. Hermans, A.C. Vandaele, M. Carleer, C. Clerbaux, P.-F. Coheur, R. Colin, S. Fally, and M. Bach, *J. Quant. Spectrosc. Radiat. Transfer* **82**, 99–117 (2003).
9. R.N. Tolchenov, J. Tennyson, S.V. Shirin, N.F. Zobov, O.L. Polyansky, and A. Maurellis, *J. Mol. Spectrosc.* **221**, No. 1, 99–105 (2003).
10. A.D. Bykov, L.N. Sinitsa, and V.I. Starikov, *Experimental and Theoretical Methods in Spectroscopy of Water Vapor Molecules* (Novosibirsk, 1999), 376 pp.
11. A.D. Bykov, O.V. Naumenko, L.N. Sinitsa, B.A. Voronin, J.-M. Flaud, C. Camy-Peyret, and R. Lanquetin, *J. Mol. Spectrosc.* **205**, 1–8 (2001).
12. H. Partridge and D.W. Schwenke, *J. Chem. Phys.* **106**, 4618–4639 (1997).
13. D.W. Schwenke and H. Partridge, *J. Chem. Phys.* **113**, 6592–6597 (2000).
14. O.L. Polyansky, A. Csazar, S.V. Shirin, N.F. Zobov, P. Barletta, J. Tennyson, D. Schwenke, and P.J. Knowles, *Science* **299**, No. 24, 539–542 (2003).
15. A.D. Bykov, O.V. Naumenko, A.M. Pshenichnikov, L.N. Sinitsa, and A.P. Shcherbakov, *Opt. Spektrosk.* **94**, No. 3, 528–537 (2003).
16. O. Naumenko, E. Bertseva, A. Campargue, and D. Schwenke, *J. Mol. Spectrosc.* **201**, 297–309 (2000).
17. E. Bertseva, O. Naumenko, and A. Campargue, *J. Mol. Spectrosc.* **221**, 38–46 (2003).
18. B.A. Voronin, *Izv. Vyssh. Uchebn. Zaved., Fiz.*, No. 3, 93–100 (1999).]
19. O.L. Polyansky, *J. Mol. Spectrosc.* **112**, 79–87 (1985).
20. J.-M. Flaud, C. Camy-Peyret, A. Bykov, O. Naumenko, T. Petrova, A. Scherbakov, and L. Sinitsa, *J. Mol. Spectrosc.* **183**, 300–309 (1997).
21. O. Naumenko and A. Campargue, *J. Mol. Spectrosc.* **221**, No. 2, 221–226 (2003).
22. J. Tennyson, N.F. Zobov, R. Williamson, and O. Polyansky, *J. Phys. and Chem. Ref. Data* **30**, No. 3, 735–831 (2001).